

Hydrolyzed protein derivatives accompanied with synergy by silylation or siliconizing

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Synopsis

Effects on hair, of a newly developed hybrid polymer consisting of hydrolyzed protein, modified with an alkyl chain and silicone was investigated. And it was confirmed that the polymer had color retention effect on dyed hair, and good substantivity contributing to hair luster, manageability, moist feel, smoothness and good combability. The above effects were displayed, especially on damaged hair.

INTRODUCTION

Many kinds of ingredients for hair treatment have been studied and developed, such as hydrolyzed proteins, silicones, oils, polymers, their derivatives and so on. Above all, hydrolyzed proteins and silicones have been widely used because the former gives hair wet feel, tenderness and gloss, and the latter gives hair also gloss, smoothness and good combability (1,2). However, both have weak points at once. Hydrolyzed protein is tightly adsorbed on hydrophilic part of hair (3), but it is easily washed off from hydrophobic part of hair, and silicone is hardly adsorbed on hydrophilic part of hair (4).

It is well known that chemical process on hair, such as permanent waving, coloring, bleaching causes hair damage which increases hydrophilic part on hair. On the other hand, hair coloring has been recently in fashion. Therefore, the ingredients suitable for damaged hair are strongly desired.

In the viewpoint of this background, we have recently developed a new polymer consisted of hydrolyzed protein, alkylmethylpolysiloxane (abbreviated as siliconized HPS, hereafter). Since siliconized HPS has both of hydrophilic part and hydrophobic part, siliconized HPS was expected to be adsorbed to damaged hair effectively, and to give properties of hydrolyzed protein and silicone to the hair at once.

Siliconized HPS was evaluated on anti-discoloring effect, improvement of moist feel, and substantivity to hair in comparison with dimethylpolysiloxane (dimethicone) and aminoethyl aminopropylsiloxane dimethylsiloxane copolymer emulsion (amodimethicone), both of which have often been added to hair treatment formulas to improve hair touch.

MATERIALS AND METHODS

The INCI name of siliconized HPS produced by Seiwa Kasei Co., Ltd. is hydrolyzed silk PG-propyl methylsilanediol crosspolymer. The structure of siliconized HPS is as shown

in Figure 1. For comparison to siliconized HPS, amodimethicone which is widely used for hair care product, and dimethicone (6000cs) which has the same range of viscosity as siliconized HPS were used.

HAIR SAMPLE

Japanese female scalp hair, which had never been processed by chemical treatment, was used. The hair was soaked in aqueous solution of sodium polyoxyethylene (3) lauryl ether sulfate for 30 minutes at 40°C. The volume of the solution was ten times more than the volume of the hair. Then the hair was rinsed with distilled running water and dried with a hair dryer.

PREPARATION OF DAMAGED HAIR (BLEACHING)

In order to keep test result in precision and reproducible, the hair was bleached mildly. For bleaching, the aqueous bleach solution that is the same volume with the hair (3% hydroperoxide, 1% ammonium hydroxide) was used. The hair was soaked in the solution for 30 minutes at 30°C and rinsed with running distilled water. Subsequently, the hair was soaked in buffer solution (pH 3.0 of 0.1 mol/L citric acid—0.2 mol/L disodium hydrogen phosphate) that volume is 10 times more than the volume of the hair for 5 minutes, and rinsed with distilled running water. Furthermore, the hair was soaked in deionized water that volume is 10 times more than the volume of the hair for 5 minutes, and dried with a hair dryer. Tresses were made from the above processed hair and were used in the following examinations.

GLOSSING EFFECT

Preparation of hair sample. Three tresses of bleached hair were prepared in 15 cm length and each hair tress was 1.5 grams weight. Those tresses were treated by spreading 2.0 grams of each hair treatment cream as shown in Table I, kept for 10 minutes at 40°C and dried with a hair dryer.

Measurement of glossing effect. For measuring gloss effect, Goniphotometer; GP-200 (Murakami color technical center) was employed.

SUBSTANTIVITY (MEASURED WITH ICP)

Preparation of hair sample. Two tresses of bleached hair were prepared in 15 cm length and 0.5 grams weight, and the tresses were treated with each hair treatment cream as shown

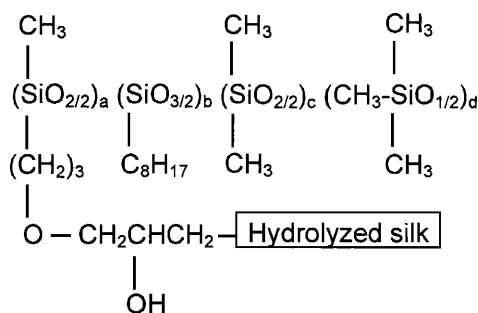


Figure 1. Structure of siliconized HPS (a, b, c and d shows degree of polymerization).

Table I
Formulas of Hair Treatment Cream (w/w%)

	Control	Siliconized HPS	Dimethicone	Amodimethicone
Isopropyl Isostearate			14.0	
Cetyl alcohol			3.0	
Steartorimonium chloride			8.0	
Emulsifying polymer* ¹	3.0	3.0	3.0	3.0
Siliconized HPS	—	1.0	—	—
Dimethicone	—	—	1.0	—
Amodimethicone	—	—	—	1.0
Water	qs 100.0	qs 100.0	qs 100.0	qs 100.0

*¹ Mixture of sodium acrylate/acryloyldimethitaurate copolymer and isohexadecane and Polysorbate 80 (Simulgel EG, Seppic, France)

in Table II. One gram of correspond hair treatment was applied to each hair tress. Subsequently, each hair tress was kept for 10 minutes at 40°C on plastic film, rinsed with distilled running water for 15 seconds and dried with a hair dryer. Each treated hair tress was soaked in 30 ml of mixed solvent (chloroform: methanol = 2:1 (v/v)) for 20 minutes with agitation by ultrasonic device to extract polymers adhering to the hair surface. After evaporation of the solvent in vacuum to dryness, the residue was solved and diluted in methylisobutylketone for quantitative analysis of silicon.

Measurement of substantivity. Quantitative analysis of silicon contained in the extract from each tress was carried out with ICP (Inductively coupled plasma) photometer (model SPS1700HVR. Seiko Densi CO., Ltd.) (4), while silicon content was calculated in unit weight of siliconized HPS and dimethicone. Then, the weight per gram of hair of the substance to each tress was estimated based on both quantitative analysis of silicon and silicon content in unit weight of siliconized HPS and dimethicone.

SUBSTANTIVITY (MEASURED WITH EDS)

Preparation of hair sample. A tress of normal hair was prepared in 15 cm length and 2.0 grams weight, and the tress was treated with test formulation as shown in Table III, kept for 10 minutes at 40°C, rinsed with distilled running water for 60 seconds and dried with a hair dryer.

Measurement of substantivity. Substantivity of Siliconized HPS was confirmed by measurement of Si deposition on the hair surface. An energy-dispersive X-ray spectroscopy (model JED-2300, JEOL Ltd.) was employed for measurement of Si distribution.

Table II
Formulas of Hair Treatment Cream (w/w%)

	Siliconized HPS	Dimethicone (6000cs)	Dimethicone (10000cs)
Emulsifying polymer	3.0	3.0	3.0
Siliconized HPS	5.0	—	—
Dimethicone (6000cs)	—	5.0	—
Dimethicone (10000cs)	—	—	5.0
Water	qs 100.0	qs 100.0	qs 100.0

Table III
Test Formulation (w/w%)

Siliconized HPS	5.0
Propylene glycol	95.0

MEASUREMENT OF MOISTURIZING EFFECT

Preparation of hair sample. Three tresses of bleached hair were prepared in 15 cm length and 1.5 grams weight, and the tresses were treated by spreading of 2.0 grams weight of each hair treatment cream as shown in Table IV, kept for 10 minutes at 40°C and dried with a hair dryer. Before the water loss was measured, hair was cut in 1 cm length.

Measurement of water loss. In order to measure water loss, electric moisture balance (model: EB-330MOC, Simadzu Co., Ltd.) was employed (5). A fragment of hair (300 mg, 1 cm length) was placed on a saucer of the balance, and the change of weight by heating was recorded every 30 seconds. The sample hair was heated for the first 40 minutes at 65°C which is assumed to be the temperature in normal use of a hair dryer, and for the next 30 minutes at 180°C to evaporate whole water contained in hair (6). As shown in Figure 2, the first converging point (A) was observed between 30 and 40 minutes after starting to heat, and the second converging point (B) was observed between 60 and 70 minutes. Based on the difference of weights between A and B, the secondary transpiring moisture content was calculated according to the above equation.

MEASUREMENT OF COLOR RETENTION EFFECT

Preparation of hair sample. Two tresses of bleached hair were prepared in 15 cm length and 1.5 grams weight, and a commercially available hair dye (red color) was applied. Both the tresses were kept for 30 minutes at 40°C after application of the hair dye, and then rinsed with distilled running water. One of the tress was washed with sodium polyoxyethylen (3) laurylether sulfate (1% water solution) containing 0.1% of siliconized HPS, and the other one was washed with sodium polyoxyethylen (3) laurylether sulfate (1% water solution) without Siliconized HPS as a control for 10 minutes at 40°C with mild agitation. And each the tress was rinsed for 30 seconds with distilled running water, and dried with a hair dryer. This washing process was repeated 5 times for each the tress.

Measurement of degree of discoloring. Degree of discoloring was measured by color laser profile with use of analyzing function of laser microscope (model: VK-8500, Keyence Co., Ltd.) according to Uchida's method (7).

Table IV
Formulas of Hair Treatment Cream (w/w%)

	Control	Siliconized HPS	Dimethicone
Emulsifying polymer	3.0	3.0	3.0
Siliconized HPS	—	1.0	—
Dimethicone	—	—	1.0
Water	qs 100.0	qs 100.0	qs 100.0

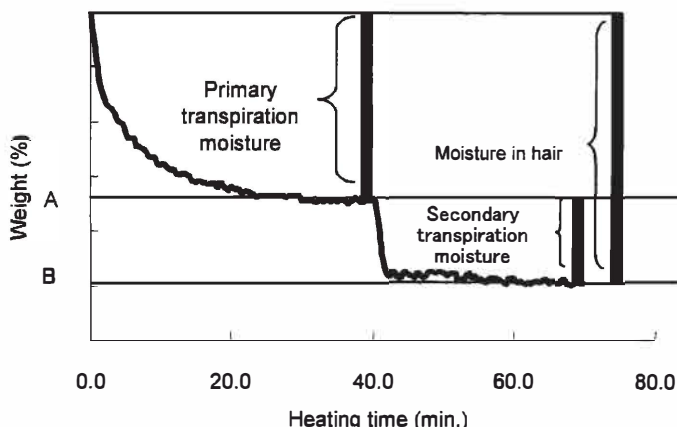


Figure 2. Illustration of transpiration moisture. Secondary transpiration moisture (%) (dry base) = $(A-B)/B \times 100$.

RESULTS AND DISCUSSION

GLOSSING EFFECT

As shown in Figure 3, Siliconized HSP was superior to give gloss on hair to dimethicone or amodimethicone.

SUBSTANTIVITY (MEASURED WITH ICP)

Quantitative analysis for silicon of siliconized HPS adsorbed to hair showed that the substantivity of siliconized HPS to hair was twice as much as dimethicone (Figure 4). This result suggested siliconized HPS was adsorbed more than dimethicone to damaged hair which has hydrophilic protein part.

SUBSTANTIVITY (MEASURED WITH EDS)

Figure 5 shows SEM photo and distribution map of Si. The result indicated Si in the hair

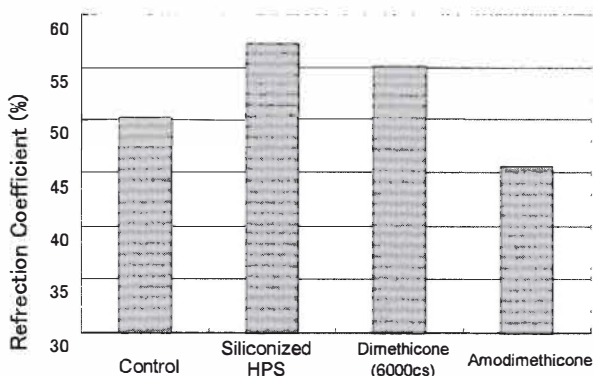


Figure 3. Illustration of transpiration moisture.

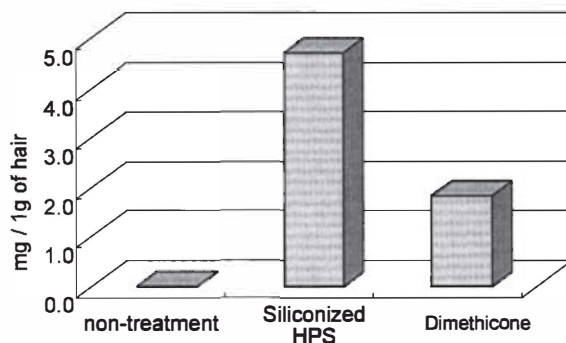


Figure 4. Results of quantitative analysis for silicon of siliconized HPS adsorbed to hair.

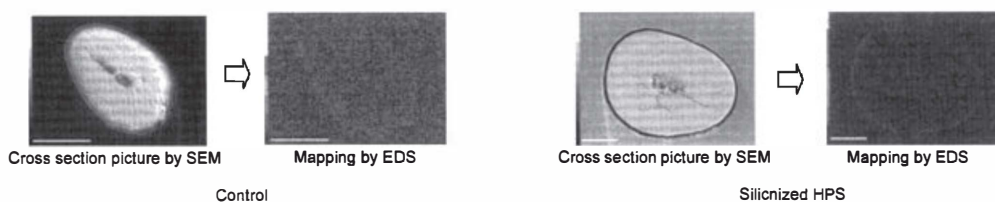


Figure 5. Cross section picture and mapping picture.

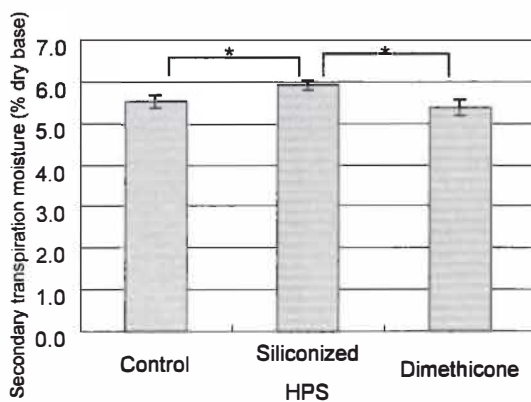


Figure 6. Comparison of secondary transpiration moisture content. $*p < 0.01$ (paired t -test).

conditioner contained siliconized HPS was especially adsorbed on cuticle edge that is easily damaged causing to be hydrophilic by bleaching.

MEASUREMENT OF MOISTURIZING EFFECT

As shown in Figure 6, the highest secondary transpiration moisture content was the hair treated with siliconized HPS treatment cream. This fact suggested that the increased moisture was carried by the hydrolyzed silk protein and quasi-obstruent film made by alkyl and silicone chain functioned to lock the moisture inside of the hair. And the film prevented hair from losing water even at 65°C. Siliconized HPS was effective enough

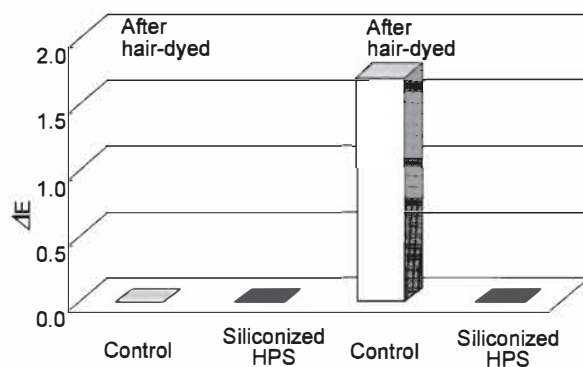


Figure 7. Discoloring degree of hair treated.

to give both wettability and moisture feel to hair which was so damaged as to be easily dried up by a hair dryer.

MEASUREMENT OF ANTI-DISCOLORING EFFECT

Figure 7 displays ΔE value of dyed hair tresses before and after shampooing 5 times. ΔE value of the hair treated with siliconized HPS hair treatment cream was not changed so much. On the contrary, the value of ΔE which was treated with control hair treatment cream showed 1.7 point of color fading.

Siliconized HPS brought anti-discoloring effect to hair. We consider that hydrolyzed protein part was adsorbed to the damaged hair surface which had been highly hydrophilic, and the rest of the part of siliconized HPS made film on the hair surface which prevented the color pigments from being washed off.

CONCLUSIONS

Siliconized HPS prevented dyed hair from discoloring and improved moist feel on hair. In addition, substantivity of siliconized HPS to damaged hair was superior to that of dimethicone and these effects were demonstrated especially in damaged hair study.

Effects of siliconized HPS on hair were due to such a unique structure which contained both hydrophobic and hydrophilic parts. We had concluded that siliconized HPS was one of useful ingredient for damaged hair.

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